

Concrete based on cement is broadening in application and increasing in quantity each year. Low-heat-hardening, quick or retarded hardening, low and high density prestressed concrete beams give greater strength and save steel. The Portland Cement Association, which has offices in many cities, will furnish extensive data on uses.

OTHER CEMENTS

For many corrosive conditions portland cement is unsuitable. Hence many special cements have been developed, of which some are industrially important. The types of special cements based on organic plastics, known as *adhesives*, are presented in Chap. 25, along with glues.

POZZOLANS. Since the beginning of the Christian era, the Italians have successfully employed pozzolan cement, made by grinding 2 to 4 parts of a pozzolan with 1 part of hydrated lime. A pozzolan is a material which is not cementitious in itself but which becomes so upon admixture with lime. The early strength of such a cement is lower than that of portland cement, but within a year the strengths are equal. The advantage of this cement is that it resists the corrosive action of saline solutions and seawater much better than does portland cement.

HIGH ALUMINA CEMENTS. High-alumina cement, essentially a calcium aluminat cement, is manufactured by fusing a mixture of limestone and bauxite, the latter usually containing iron oxide, silica, magnesia, and other impurities. It is characterized by a very rapid rate of development of strength and superior resistance to seawater and sulfate-bearing water.

SILICATE CEMENTS. Silica-filled, chemically setting silicate cements withstand all concentrations of inorganic acids except hydrofluoric. They are not suitable at pH values above 7 or in the presence of crystal-forming systems. Usually 2 parts by weight of finely divided silica powder is used to 1 part of sodium silicate (35 to 40°Bé). Two typical applications are the joining of bricks in chromic acid reaction tanks and in alum tanks.

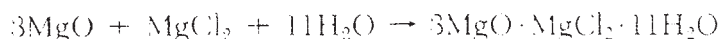
SULFUR CEMENTS. Since 1900, sulfur cements have been available commercially as simple mixtures of fillers, and since 1930, as homogeneous plasticized filled sulfur ingots possessing low coefficients of expansion. Sulfur cements are resistant to nonoxidizing acids and salts but should not be used in the presence of alkalis, oils, greases, or solvents. The crystalline change in sulfur structure at 93°C. limits their use. Thiokol-plasticized silica-filled sulfur cements have been accepted as a standard material for joining bricks, tile, and cast-iron pipe.

POLYMER CONCRETE. Polymer concretes are really polymer-bonded concretes and usually contain no portland cement. These products consist of aggregate plus resins such as epoxy, methyl methacrylate, or polyester. Each of the resins imparts specific properties to the concrete such as rapid curing, corrosion resistance, or high compressive strength. As yet, these concretes are much higher in price than regular portland cement concrete, but as specialty products for specific uses they are finding a market.¹⁶

MAGNESIUM OXYCHLORIDE CEMENT. This cement, discovered by the French chemist Sorel and sometimes called *Sorel's cement*, is produced by the exothermic action of a 20% solution

¹⁶*Chem. Week* 129 (21) 81 (1981).

† magnesium chloride on a blend of magnesia obtained by calcining magnesite and magnesia obtained from brines



The resulting crystalline oxychloride ($3\text{MgO} \cdot \text{MgCl}_2 \cdot 11\text{H}_2\text{O}$) contributes the cementing action to the commercial cements. The product is hard and strong but is attacked by water, which leaches out the magnesium chloride. Its main applications are as a flooring cement with an inert filler and a coloring pigment, and as a base for such interior floorings as tile and terrazzo. It is strongly corrosive to iron pipes in contact with it. Sand and wood pulp may be added as fillers. The expense of these cements restricts their use to special purposes. They do not reflect sound. They can be made sparkproof and as such have been widely employed in ordnance plants. The magnesia used may contain small amounts of calcium oxide, calcium hydroxide, or calcium silicates, which during the setting process increase the volume changes, thus decreasing strength and durability. To eliminate this time effect, hydrated magnesium sulfate ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$) or 10% finely divided metallic copper is added to the mixture. The use of copper powder not only prevents excessive expansion, but greatly increases water resistance, adhesion, and dry and wet strength over that of ordinary magnesium oxychloride cement. Such a product even adheres in thin layers to concrete and serves to seal cracks therein.

LIME

HISTORICAL. The manufacture of lime and its application can be traced back to the Roman, Greek, and Egyptian civilizations, but the first definite written information concerning lime was handed down from the Romans. In his book "De Architectura," Marcus Pollio, a celebrated engineer and architect who lived during the reign of Augustus (27 B.C. to A.D. 14), deals quite thoroughly with the use of lime for mortar involved in the construction of harbor works, pavements, and buildings. In colonial America the crude burning of limestone was one of the initial manufacturing processes engaged in by the settlers; they used "dugout" kilns built of ordinary brick or masonry in the side of a hill, with a coal or wood fire at the bottom, and a firing time of 72 h. These kilns can still be seen in many of the older sections of the country. It was not until recent years that, under the influence of chemical engineering research, the manufacture of lime developed into a large industry under exact technical control, resulting in uniform products at lower cost.

USES AND ECONOMICS. Lime itself may be used for medicinal purposes, insecticides, plant and animal food, gas absorption, precipitation, dehydration, and causticizing. It is employed as a reagent in the sulfite process for papermaking, dehairing hides, the manufacture of high-grade steel and cement, water softening, recovery of by-product ammonia, and the manufacture of soap, rubber, varnish, refractories, and sand-lime brick. Lime is indispensable for use with mortar and plaster and serves as a basic raw material in the production of calcium salts and for improving the quality of certain soils. Either directly or indirectly, limestone and lime are employed in more industries than any other natural substance. Lime production was 18.3×10^6 t in 1972 with a value of \$341.1 million. Production for 1979 was 19×10^6 t.

Lime is usually sold as a high-calcium quicklime containing not less than 90 percent CaO and from 0 to 5 percent magnesia; small percentages of calcium carbonate, silica, alumina, and ferric oxide are present as impurities. The suitability of lime for any particular use

depends on its composition and physical properties, all of which can be controlled by the selection of the limestone and the details of the manufacturing process. Much lime must be finely ground before use.¹⁷

Depending on composition, there are several distinct types of limes. Hydraulic limes are obtained from the burning of limestone containing clay, and the nature of the product obtained after contact with water varies from putty to set cement. High-calcium-content limes harden only with the absorption of carbon dioxide from the air, which is a slow process. hydraulic limes also harden slowly, but they can be used under water. For chemical purposes high-calcium is required, except for the sulfite paper process, where magnesian lime works better. Although in many sections of the country high-calcium lime is preferred by the building industry for the manufacture of mortar lime plaster, there are places where limestone containing magnesium is burned or where even dolomitic stone is calcined. Typical compositions of such stones are from 35 to 45% CaO and from 10 to 25% MgO. These products, called *magnesian* limes, or dolimes,¹⁸ are favored by some plasterers, who claim they work better under the trowel. In the metallurgical field, "refractory lime," as dead-burned dolomite or as raw dolomite, is employed as a refractory patching material in open-hearth furnaces; it is applied between heats to repair scored and washed spots on the bottom of the furnace. *Hydrated lime* is finding increased favor in the building trades over the less stable quicklime, despite its increased weight. Quicklime is almost invariably slaked or hydrated before use. Because of the better slaking and the opportunity to remove impurities, factory hydrate is purer and more uniform than slaked lime prepared on the job.

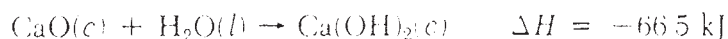
MANUFACTURE. Lime has always been a cheap commodity because limestone deposits are readily available in so many sections of the United States. It is produced from limestone near centers of consumption so that freight costs are low. The carbonates of calcium and magnesium are obtained from deposits of limestone, marble, chalk, dolomite, or oyster shells. For chemical usage, a rather pure limestone is preferred as a starting material because of the high-calcium lime that results. Quarries are chosen which furnish a rock that contains as impurities low percentages of silica, clay, or iron. The lumps sometimes found in "overburned" or dead-burned lime result from changes in the calcium oxide itself, as well as from certain impurities acted upon by excess heat, recognized as masses of relatively inert, semivitrified material. On the other hand, it often happens that rather pure limestone is calcined insufficiently, and lumps of calcium carbonate are left in the lime. This lime is called "underburned" lime.

The reactions involved are:

CALCINATION



HYDRATION



During calcination the volume contracts, and during hydration it swells. For calcination the average fuel ratios, using bituminous coal, are 3.23 kg of lime for 1 kg of coal in shaft kilns

¹⁷Perry, p. 8-50.

¹⁸To prevent "popping out" the MgO must be completely hydrated, e.g., by steam hydration at 160°C and under such pressure as 413 kPa.

and 3.37 kg in rotary kilns. As is shown above, the calcination reaction is reversible. Below 650°C the equilibrium decomposition pressure of CO_2 is quite small. Between 650 and 900°C the decomposition pressure increases rapidly and reaches 101 kPa at about 900°C.¹⁹ In most operating kilns the partial pressure of CO_2 in the gases in direct contact with the outside of the lumps is less than 101 kPa; therefore initial decomposition may take place at temperatures somewhat less than 900°C. The decomposition temperature at the center of the lump is probably well above 900°C, since there the partial pressure of the CO_2 not only is equal to or near the total pressure, but also must be high enough to cause the gas to move out of the lump, where it can pass into the gas stream. The total *heat* required for *calcining* per ton of lime produced may be divided into two parts: sensible heat to raise the rock to decomposition temperature, and latent heat of dissociation. Theoretical heat requirements per metric ton of lime produced, if the rock is heated only to a calcining temperature of 900°C, are approximately 1.4 GJ for sensible heat and 2.7 GJ for latent heat. Actual calcining operations, because of practical considerations, e.g., lump size and time, require that the rock be heated to between 1200 and 1300°C, thereby increasing sensible-heat requirements by about 370 kJ. Thus practical heat requirements are approximately 4 GJ/t of lime produced in a vertical kiln. About 40 percent is sensible heat; the rest is latent heat of decomposition.

The sequence of steps connected with manufacturing in the kiln shown in Figs. 10.3 and 7.4 are:

Blasting down of limestone from a quarry face or occasionally from underground veins.
Transportation from the quarry to mills, generally by an industrial railroad.

¹⁹ECT, 3d ed., vol. 14, 1981, pp. 615–646.

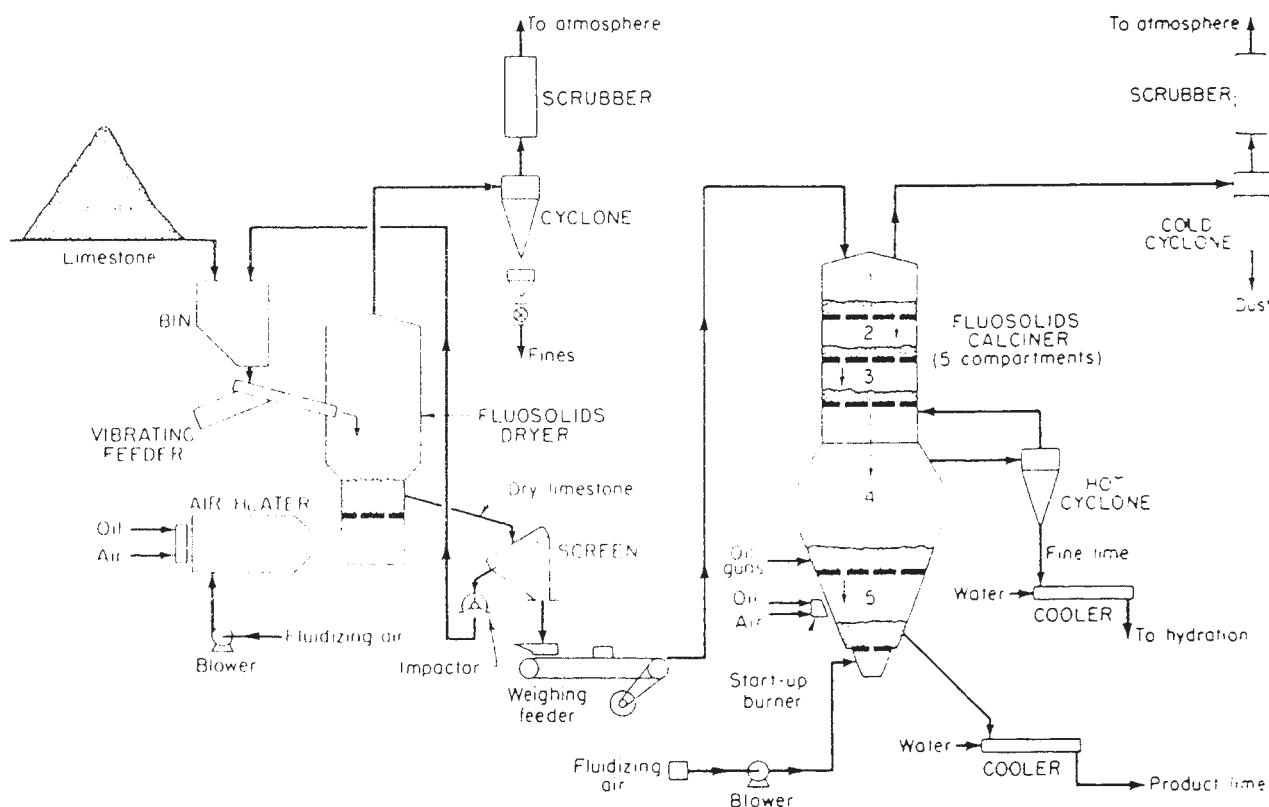


Fig. 7.3. Dorco FluoSolids system for producing lime from pulverized limestone or calcium carbonate sludge. This is a five-compartment reactor as labeled. (Dorr-Oliver, Inc.)

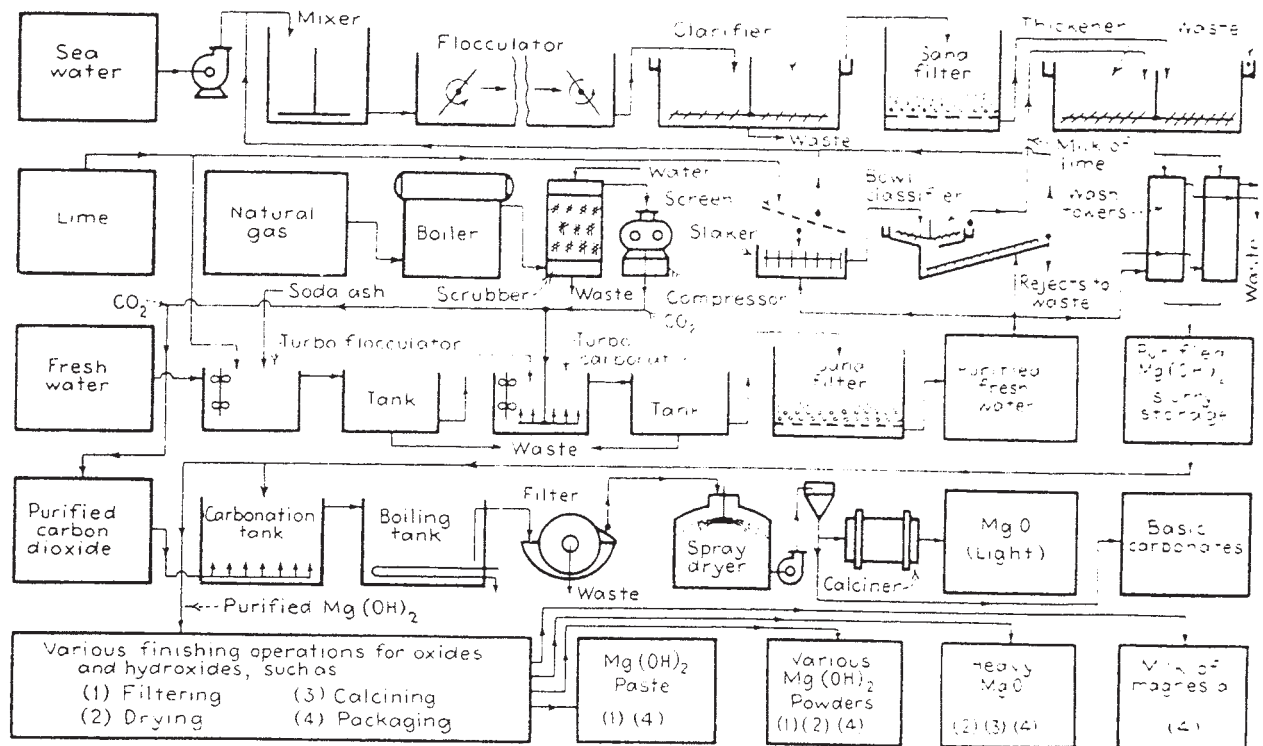


Fig. 7.4. Purified magnesium compounds from seawater at South San Francisco. (Merck & Co.)

Crushing and sizing of the stone in jaw and gyratory crushers.²⁰

Screening to remove various sizes (e.g., a 10- to 20-cm stone implies that all pieces passing a 10-cm screen and retained on an 20-cm screen have been separated out).

Carting of large stones to top of vertical kilns.

Conveying of small rocks to a rotary kiln.

Conveying of fines to a pulverizer to make powdered limestone for agricultural and other demands.

Burning of limestone according to size, in vertical kilns to give lump lime, or in horizontal rotary kilns to furnish fine lime.

Packaging of the finished lime in barrels (80 or 120 kg) or sheet-iron drums or conveying it to a hydrator.

Hydration of the lime.

Packaging of slaked lime in 25-kg paper bags.

Almost all lime produced in the United States is calcined in *rotary kilns*. These kilns may have a capacity of up to 1600 t/day. In 1965 the largest rotary kiln would only produce 600 t/day. The diameters are usually about 5 m with lengths of 45 to 60 m. The diameter-to-length ratio is 1:10 to 1:12.

The exterior of the rotary kiln is heavy steel and the interior is lined with refractory brick. The kilns have a slope of 4 percent and rotate counterclockwise at a speed of 0.6 to 2 rpm. The limestone is preheated to reduce fuel consumption and may be as hot as 980°C when it enters the kiln. Heat for the preheater is furnished by the hot air and gases from the kiln. These kilns operate on fines or small lumps of limestone or marble, or moist precipitated calcium carbonate sludge, any of which would block the efficient and uniform burning of the fuel in a vertical kiln. Rotary kilns have the highest capacity and produce lime of the most

²⁰Perry, p. 8-16.

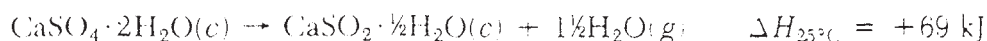
uniform quality but require the greatest capital investment, have a high energy consumption, and need very expensive dust-collecting systems.²¹

Vertical kilns have hundreds of designs and are used largely outside of the United States as American consumers prefer the better quality of lime produced by the rotary kilns. The main characteristic that all vertical kilns have in common is four imaginary zonal sections: (1) storage, (2) preheating, (3) calcining, and (4) cooling. The limestone is charged into the top of the kiln and cooled lime is discharged at the bottom. An improved vertical kiln is the Maerz-Ofenbau double shaft regenerative kiln,²² which increases production and uses less energy. The only one in operation in the United States is at Douglas, Ariz. and is heated with natural gas. This kiln consists of two shafts connected at the lower third of the structure. The fuel is fed alternately to the shafts at 10- to 12-min intervals. Approximately 24 h elapse until the cooled lime is removed. This alternate calcining prevents overburning of the lime and produces lime equal in quality to that produced by rotary kilns but uses only about half the fuel.

Dorrco FluoSolids kiln is a vertical kiln but operates on a different principle. The feed is granular (0.225 to 2.4 mm) material and fluidized by a carefully controlled air and exhaust-gas mixture. This is an extension of the fluidized bed reactor used so widely in the petroleum industry.

GYPSUM

Gypsum is a mineral that occurs in large deposits throughout the world.²³ It is hydrated calcium sulfate, with the formula $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$. When heated slightly, the following occurs:



If the heating is at a higher temperature, gypsum loses all its water and becomes anhydrous calcium sulfate, or *anhydrite*. Calcined gypsum (the half water salt) can be made into wall plaster by the addition of a filler material such as asbestos, wood pulp, or sand. Without additions, it is plaster of paris and is used for making casts and for plaster; it is hydraulic and hardens under water, but is also slightly soluble in water, hence must not be used in moist exposures.

CALCINATION OF GYPSUM. The usual method of calcination of gypsum consists in grinding the mineral and placing it in large calciners holding 9 to 22 t. The temperature is raised to about 120 to 150°C, with constant agitation to maintain a uniform temperature. The material in the kettle, known to the public as *plaster of paris* and to the manufacturer as *first-settle plaster*, may be withdrawn and sold at this point, or it may be heated further to 190°C to give a material known as *second-settle plaster*. First-settle plaster is approximately the half hydrate $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$, and the second form is anhydrous. Practically all gypsum plaster sold is in the form of first-settle plaster mixed with sand or wood pulp. The second form is used

²¹ECT, 3d ed., vol. 14, 1981, p. 362; Robertson, U.S. Lime Division Expands Its Nelson, Arizona Plant, *Rock Prod.* 81 (10) 59 (1978).

²²Robertson, Double-Shaft Regenerative Kiln, *Rock Prod.* 83 (10) 50 (1980).

²³ECT, 3d ed., vol. 4, 1978, pp. 437-448.

in the manufacture of plasterboard and other gypsum products. Gypsum may also be calcined in rotary kilns similar to those used for limestone.

HARDENING OF PLASTER. This hardening of plaster is essentially a hydration chemical conversion, as represented by the equation



This equation is the reverse of that for the dehydration of gypsum. The plaster sets and hardens because the liquid water reacts to form a solid, crystalline hydrate. Hydration with liquid water takes place at temperatures below about 99°C and thus the gypsum must be heated above 99°C for practical dehydration. Commercial plaster usually contains some glue in the water used or a material such as hair or tankage from the stockyards to retard the setting time in order to give the plasterer opportunity to apply the material.

MISCELLANEOUS CALCIUM COMPOUNDS

CALCIUM CARBONATE. Calcium carbonate is a very widely used industrial chemical, in both its pure and its impure state. As marble chips, it is sold in many sizes as a filler for artificial stone, for the neutralization of acids, and for chicken grit. Marble dust is employed in abrasives and in soaps. Crude, pulverized limestone is used in agriculture to "sweeten" soils in large tonnage. Some pulverized and levigated limestone, to replace imported chalk and whiting, is manufactured quite carefully from very pure raw material and is finding acceptance.²⁴ *Whiting* is pure, finely divided calcium carbonate prepared by wet grinding and levigating natural chalk. Whiting mixed with 18% boiled linseed oil yields *putty*, which sets by oxidation and by formation of the calcium salt. Much whiting also is consumed in the ceramic industry. Precipitated, or artificial, whiting arises through precipitation, e.g., from reacting a boiling solution of calcium chloride with a boiling solution of sodium carbonate or passing carbon dioxide into a milk-of-lime suspension. Most of the latter form is used in the paint, rubber, pharmaceutical, and paper industries.

CALCIUM SULFIDE. Calcium sulfide is made by reducing calcium sulfate with coke. Its main use is as a depilatory in the tanning industry and in cosmetics. In a finely divided form it is employed in luminous paints. Polysulfides, such as CaS_2 and CaS_5 , made by heating sulfur and calcium hydroxide, are consumed as fungicides.

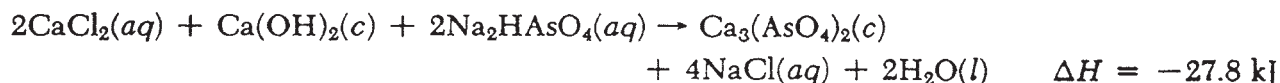
HALIDE SALTS. Calcium chloride is obtained commercially as a by-product of chemical manufacture and from natural brines which contain more or less magnesium chloride. In 1980 730,000 t was sold. Its main applications are to lay dust on highways (because it is deliquescent and remains moist), to melt ice and snow on highways in winter, to thaw coal, in oil and gas well fluids, and as an antifreeze for concrete.

Calcium bromide and iodide have properties similar to those of the chloride. They are prepared by the action of the halogen acids on calcium oxide or calcium carbonate. They are sold as hexahydrates for use in medicine and photography. Calcium fluoride occurs naturally

²⁴Rose, *Condensed Chemical Dictionary*, 7th ed. New York, Reinhold, 1966.

as a fluorspar (Chap. 20). Calcium hypochlorite [$\text{Ca}(\text{OCl})_2$] is prepared by the action of chlorine on calcium hydroxide (Chap. 10). Its primary use is for swimming pool sanitation.

CALCIUM ARSENATE. Calcium arsenate is produced by the reaction of calcium chloride, calcium hydroxide, and sodium arsenate or lime and arsenic acid:



Some free lime is usually present. Calcium arsenate is used extensively as an insecticide and as a fungicide.

CALCIUM ORGANIC COMPOUNDS. Calcium acetate and lactate are prepared by the reaction of calcium carbonate or hydroxide with acetic or lactic acid. The *acetate* was formerly pyrolyzed in large amounts to produce acetone, but now it is employed largely in the dyeing of textiles. The *lactate* is sold for use in medicines and in foods as a source of calcium; it is an intermediate in the purification of fermentation lactic acid. *Calcium soaps* such as stearate, palmitate, and the abietate are made by the action of the sodium salts of the acids on a soluble calcium salt such as the chloride. These soaps are insoluble in water but are soluble in hydrocarbons. Many of them form jellylike masses, which are constituents of greases. These soaps are used mainly as waterproofing agents.

MAGNESIUM COMPOUNDS²⁵

Magnesium is one of the most widely distributed elements, occupying 1.9 percent of the earth's crust. It occurs usually in the chloride, silicate, hydrated oxide, sulfate, or carbonate, in either a complex or in simple salts. Magnesium metal first became available commercially shortly before 1914, when the Germans initiated production, using magnesium chloride from the Stassfurt deposits as the raw material. Table 7.11 gives recent production figures for magnesium and its compounds.

RAW MATERIALS AND USES. Important domestic sources of magnesium salts are seawater, certain salt wells, bitterns from sea brine, salines, dolomite, and magnesite (MgCO_3). Magnesium compounds are used extensively for refractories and insulating compounds, as well as in the manufacture of rubber, printing inks, pharmaceuticals, and toilet goods.

Magnesium oxide is finding new important uses in air pollution control systems for the removal of sulfur dioxide from stack gases.²⁶ New uses for magnesium may mean major growth for this metal in the future.

MANUFACTURE. The manufacture of magnesium compounds from salines has long been successful in Germany. As a result of thorough physical and chemical study, the International Minerals and Chemical Corp. is making magnesium chloride from langbeinite, crystallizing

²⁵ECT, 3d ed., vol. 14, 1981, pp. 615-646.

²⁶Shah, MgO Absorbs Stack Gas SO_2 , *Chem. Eng.* 79 (14) 80 (1974).

Table 7.11 Magnesium and Magnesium Compounds Statistics 1981 (thousands of metric tons and thousands of dollars)

	Quantity	Value
Used in the United States		
Caustic-calcined and specified (USP and technical) magnesia	145	55.420
Refractory magnesia	560	146.963
Dead-burned dolomite	395	23.759
U.S. Production		
Primary magnesium	130	
Secondary magnesium	42	
World Production		
Primary magnesium	298	

SOURCE: *Minerals Yearbook 1981*, vol. 1, Dept. of the Interior, 1982, pp. 298, 555, 565.

out carnallite ($\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$). This double salt is decomposed to furnish magnesium chloride.

The production of magnesium compounds by separation from aqueous solutions may be divided into four processes:

1. Manufacture from seawater without evaporation, using seawater and lime as the principal raw materials. This is done by Dow Chemical Co. at Freeport and Velasco, Tex.,²⁷ and by Merck & Co. at South San Francisco (Fig. 7.4). The Dow Chemical Co. of Freeport and Velasco, Tex., manufactures magnesium hydrate, which is dissolved in 10% hydrochloric acid to furnish a solution of magnesium chloride. This is concentrated in direct-fired evaporators, followed by shelf dryers, producing 76% magnesium chloride ready to be delivered to electrolytic cells to make metallic magnesium (Chap. 11).

2. Manufacture from bitterns or mother liquors from the solar evaporation of seawater for salt.

3. Manufacture from dolomite and seawater, with factories operating at Moss Landing, Calif., by Kaiser Chemical Division, as depicted by the flowchart in Fig. 10.5. At Pascagoula, Miss. Corning Glass Works obtains magnesium salts from similar sources.

4. Manufacture from deep-well brines. Production is being increased by Dow Chemical Co. with Michigan brines, analyzing 20.7% CaCl_2 , 3.9% MgCl_2 , 5.73% NaCl . The small amount of bromine is freed by chlorine and, following its removal, the $\text{Mg}(\text{OH})_2$ is precipitated by pure slaked dolime (calcined dolomite). The $\text{Mg}(\text{OH})_2$ produced is settled, filtered, and washed to provide a slurry containing 45% $\text{Mg}(\text{OH})_2$ of high purity. This is calcined at high temperatures to produce periclase, a sintered MgO nodule used in making refractory brick.

A typical analysis of seawater is given in Table 7.12. The production of magnesium compounds from seawater is made possible by the almost complete insolubility of magnesium hydroxide in water. Success in obtaining magnesium compounds by such a process depends upon

1. Means to soften the seawater cheaply, generally with lime or calcined dolomite
2. Preparation of a purified lime or calcined dolomite slurry of proper characteristics

²⁷*Chem. Week* 127 (8) 22 (1980).

3. Economical removal of the precipitated hydroxide from the large volume of water.
4. Inexpensive purification of the hydrous precipitates.
5. Development of means to filter the slimes.

The reactions are

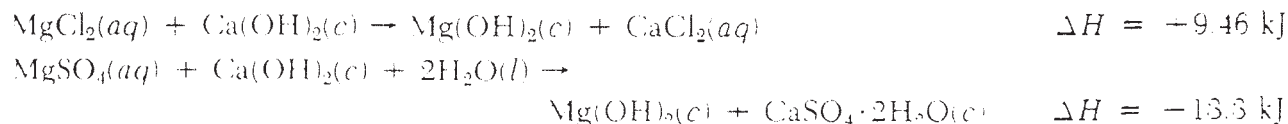
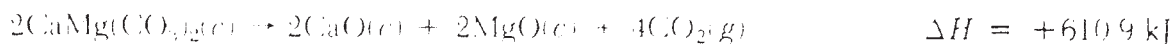


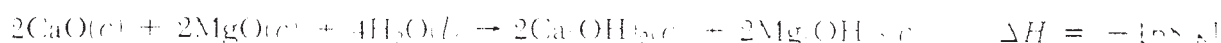
Figure 7.5 shows a flowchart of magnesium products from seawater. Figure 7.4 presents a flowchart for producing such fine chemicals and pharmaceuticals as milk of magnesia and several basic magnesium carbonates such as $3\text{MgCO}_3 \cdot \text{Mg(OH)}_2 \cdot 4\text{H}_2\text{O}$ for tooth powders and antacid remedies, for coating table salt to render it noncaking, and for paint fillers. Certain of these basic magnesium compounds are also employed with rubber accelerators. Where calcined dolomite is used instead of calcium carbonate, only about one-half of the magnesia must come from the magnesium salts in the seawater.²⁸ Consequently, the size of the plant is much smaller and the cost of production probably lower. The Mg(OH)_2 may be calcined at about 700°C to active, chemical MgO , or at about 1475 to 1650°C to periclase MgO . This Mg(OH)_2 is quite different from the slow-settling Mg(OH)_2 precipitated by a soluble alkali or by milk of lime.

The reactions, as illustrated in the flowchart in Figs. 7.4 and 7.5, are the following

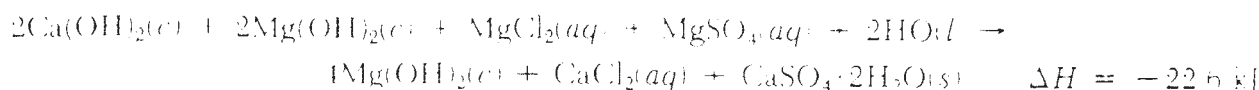
CALCINATION



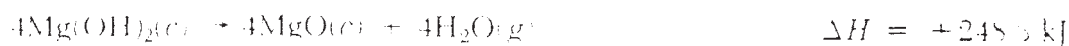
SLAKING



PRECIPITATION



CALCINATION



HYDROCHLORINATION



only about 7 percent of the slaked calcined dolomite is needed for softening the seawater; the rest is used for precipitating crystalline Mg(OH)_2 which is settled, filtered, and washed. This hydroxide is converted to other products.

²⁸Seawater normally has 2.2 g/L of equivalent MgO , actually present as MgCl_2 and MgSO_4 . Hence 1 t of MgO theoretically requires 375 m^3 of seawater. Based on a 70 percent yield, about 538 m^3 would be pumped if all the magnesia came from seawater, or about half that amount if dolomite were used.

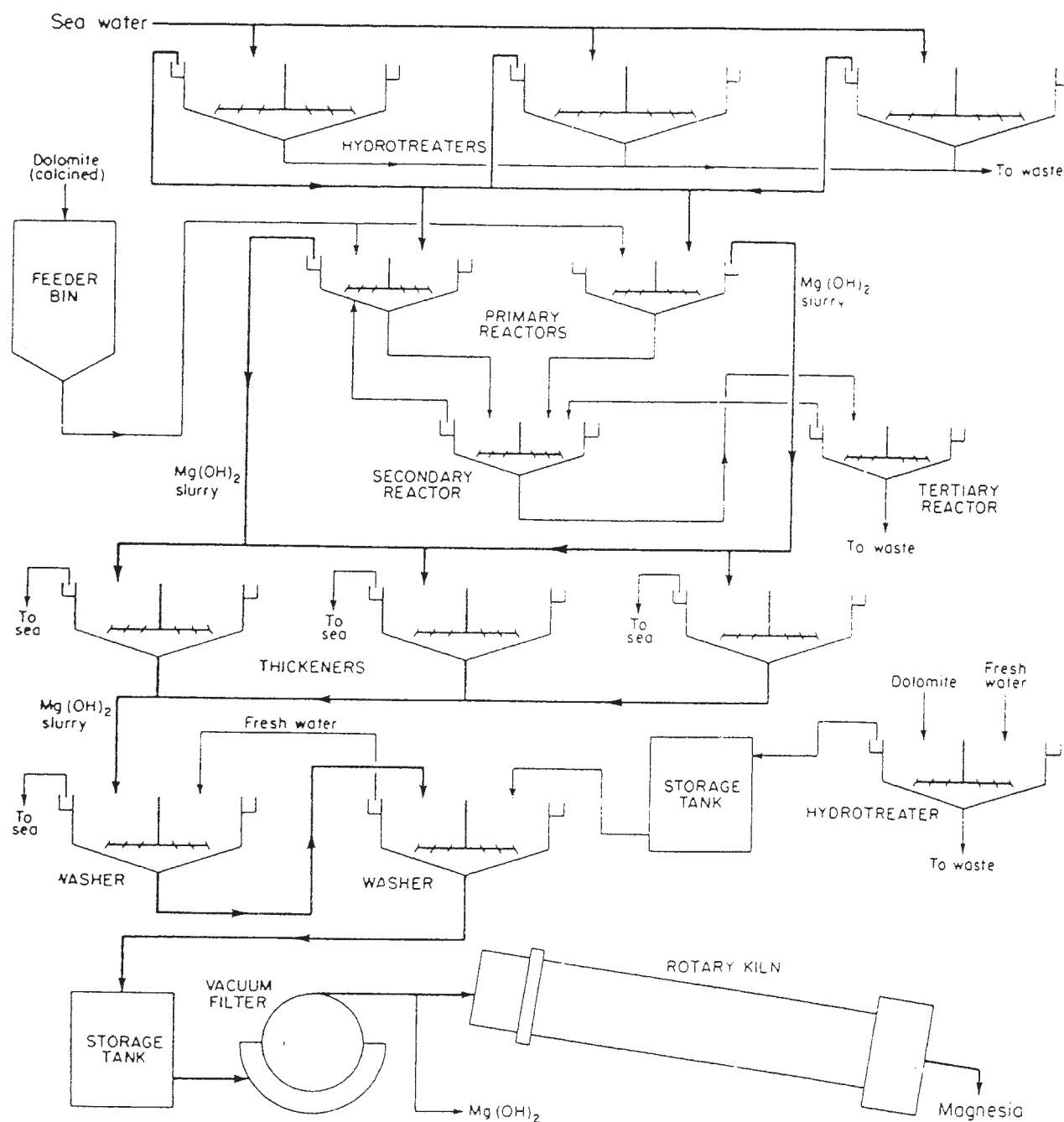


Fig. 7.5. Flowchart for $Mg(OH)_2$ from seawater and dolomite. (Kaiser Chemical Co., Moss Landing, Calif.)

Table 7.12 Composition of Seawater (in grams per liter of sp gr 1.024)

NaCl	27.319	$Ca(HCO_3)_2$	0.178
$MgCl_2$	4.176	K_2SO_4	0.869
$MgSO_4$	1.668	B_2O_3	0.029
$MgBr_2$	0.076	SiO_2	0.008
$CaSO_4$	1.268	Iron and alumina (R_2O_3)	0.022

MAGNESIUM CARBONATES. These vary from dense MgCO_3 used in magnesite bricks to the very low density $4\text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2 \cdot 5\text{H}_2\text{O}$ and $3\text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2 \cdot 3\text{H}_2\text{O}$ once employed for insulation. There are also other basic carbonates on the market with variations in adsorptive index and apparent density. Many of these are employed as fillers in inks, paints, and varnishes (see Fig. 7.4 for manufacture).

OXIDES AND HYDROXIDE OF MAGNESIUM. On heating magnesium carbonate or hydroxide, magnesium oxide (MgO) is formed. This oxide has many uses, e.g., in the vulcanization of rubber, as a material for making other magnesium compounds, as an insulating material, as a refractory material, and as an abrasive. The magnesium hydroxide is principally made directly from seawater, as Figs. 7.4 and 7.5 show. The seawater is screened and pumped to a battery of three 38-m-diameter concrete hydrotreaters. Here enough calcined dolomite is added (not shown in the figure) to pretreat or soften the seawater by precipitating carbonates, which are removed by rakes. The softened seawater flows to two primary reactors 25 m in diameter into which is fed the main addition of calcined dolomite to precipitate the $\text{Mg}(\text{OH})_2$, which in a fine suspension overflows into three parallel-flow 76-m-diameter thickeners, the overflow being returned to the sea. The underflow of the two primary reactors is fed first into an 18-m-diameter secondary reactor and then into the tertiary reactor, from which the three-times-reacted residue, now largely silicious material and unreacted dolomite, is wasted. The thickened $\text{Mg}(\text{OH})_2$ slurry from the three 76-m thickeners is united and washed with calcined-dolomite-softened fresh water in two 76-m thickeners in series. The $\text{Mg}(\text{OH})_2$ underflow is conducted through storage to a 4- by 5.5-m rotary filter operating at about 26.7-kPa vacuum and delivering about 50% $\text{Mg}(\text{OH})_2$. This is removed from the rotary filter and conveyed either to sale or to one of three rotary kilns operating up to 1800°C to give different grades of MgO . After purification this is the well-known milk of magnesia used in medicine. *Magnesium peroxide* is available from the reaction of magnesium sulfate and barium peroxide. It is employed as an antiseptic and a bleaching agent.

MAGNESIUM SULFATE. Magnesium sulfate is prepared by the action of sulfuric acid on magnesium carbonate or hydroxide. It is sold in many forms, one of which is the hydrate $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, long known as *Epsom salts*. The less pure material is used extensively as sizing and as a fireproofing agent.

MAGNESIUM CHLORIDE. Magnesium chloride is made from hydrochloric acid and magnesium hydroxide as described above. The compound itself much resembles calcium chloride and has many of the same uses. In addition, it finds application in ceramics, in the sizing of paper, and in the manufacture of oxychloride cement. Its principal use is in the making of metallic magnesium.

MAGNESIUM SILICATES. A consideration of magnesium silicates includes two widely used naturally occurring compounds, asbestos and talc. Asbestos is a magnesium silicate mixed with varying quantities of silicates of calcium and iron. It is a fibrous, noncombustible mineral and is used in the manufacture of many fireproof and insulating materials. Because of the cancer-causing characteristics of its fibers, government regulations have sharply reduced its use. Talc is a rather pure magnesium silicate in the form of $3\text{MgO} \cdot 4\text{SiO}_2 \cdot \text{H}_2\text{O}$, found naturally in soapstone. It is employed as a filler in paper and plastics and in many cosmetic and toilet preparations.

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Chapter 8

Glass Industries

Glass may be defined, *physically*, as a rigid, undercooled liquid having no definite melting point and a sufficiently high viscosity (greater than 10^{12} Pa·s) to prevent crystallization; and *chemically*, as the union of the nonvolatile inorganic oxides resulting from the decomposition and fusion of alkali and alkaline earth compounds, sand, and other glass constituents, ending in a product with *random* atomic structure. Glass is a *completely vitrified* product, or at least such a product with a relatively small amount of nonvitreous material in suspension.

Glass has many uses because of its transparency, high resistance to chemical attack, effectiveness as an electrical insulator, and ability to contain a vacuum. Glass is a brittle material and characteristically exhibits compressive strength much greater than its tensile strength. Strengthening techniques, most of which involve prestressing to introduce surface compression, have been developed to the point where glass can be employed in more arduous environments than previously. Approximately 800 different glass compositions are produced, some with particular emphasis on one property and some with attention to a balanced set of properties.

HISTORICAL.¹ As in the case of many other commonplace materials of our modern civilization, the discovery of glass is very uncertain. One of the earliest references to this material was made by Pliny, who related the familiar story of how ancient Phoenician merchants discovered it while cooking a meal in a vessel placed accidentally upon a mass of trona at the seashore. The union of the sand and alkali caught the men's attention and led to subsequent efforts at imitation. As early as 6000 or 5000 B.C. the Egyptians were making sham jewels of glass which were often of fine workmanship and marked beauty. Window glass is mentioned as early as A.D. 290. The hand-blown window-glass cylinder was invented by a twelfth-century monk. During medieval times Venice enjoyed a monopoly as the center of the glass industry. It was not until the fifteenth century, however, that the use of window glass became general. No glass was made in either Germany or England until the sixteenth century. Plate glass appeared as a rolled product in France in 1688.

Glassworks in the United States were founded in 1608 at Jamestown, Va., and in 1639 at Salem, Mass. For more than three centuries thereafter, the processes were practically all manual and rule of thumb. From the chemical point of view, the only major improvements during this period were confined to purifying the batch materials and increasing the fuel economy. To be sure, some relations were established between the chemical composition of glasses and their optical and other physical properties but, all in all, the industry prior to 1900 was an

¹Shand, *Glass Engineering Handbook*, 2d ed., McGraw-Hill, New York, 1958; for an excellent general presentation, Stookey, Glass Chemistry as I Saw It, *CHEMTECH*, 1(8) 458 (1971).

art, with closely guarded secret formulas and empirical processes of manufacture based primarily upon experience.

In 1914 the Fourcault process for drawing a sheet of glass continuously was developed in Belgium. During the next 50 years engineers and scientists produced modifications of the flat-sheet drawing process aimed at reducing the optical distortion characteristic of sheet (window) glass and the cost of producing ground and polished plate glass. These efforts led to the most recent step forward in flat-glass production technology. Based on concepts patented in the United States in 1902 and 1905, a research group in England perfected the float glass process in the 1960s. Float glass has all but eliminated plate glass produced by other means and has invaded the market for window glass in a major way. Scientists and engineers entered the field in increasing numbers, and new products appeared as a result of intensive research. Automatic machines were invented to speed up production of bottles, light bulbs, etc. As a result, today the glass industry is a highly specialized field.

USES AND ECONOMICS. Glass and glassware production by types are shown in Table 8.1. The uses and applications of glass are very numerous, but some conception of the versatility of this material can be gained from a discussion of the various types, as presented in the rest of this chapter. Overall, glassmaking in the United States is about a \$7000 million per year industry. Automobile glass represents almost half of the flat glass produced annually. The architectural trend is toward more glass in commercial buildings and in particular colored glass.²

COMPOSITION. In spite of thousands of new formulations for glass during the past 30 years, it is worthy of note that lime, silica, and soda still form over 90 percent of all the glass of the world, just as they did 2000 years ago. It should not be inferred that there have been no important changes in composition during this period. Rather, there have been minor changes in major ingredients and major changes in minor ingredients. The major ingredients are sand, lime, and soda ash, and any other raw materials may be considered minor ingredients, even though the effects produced may be of major importance. The most important factors in making glass are viscosity of molten oxides and the relation between this viscosity and composition. Table 8.2 shows the chemical composition of various glasses.

In general, commercial glasses fall into several classes.

1. **Fused silica.** Fused silica, or vitreous silica, is made by the high-temperature pyrolysis of silicon tetrachloride or by fusion of quartz or pure sand. It is sometimes erroneously referred to as *quartz glass* and is characterized by low expansion and a high softening point

²Market for Colored Glass Accelerates, *Chem. Eng. News* 48 (5) 14 (1970).

Table 8.1 Value of Glass and Glassware Shipped (in millions of dollars)

	1972	1977
Flat glass, total	937.2	1576.6
Pressed and blown glass	1267	2120.1
Glass containers	2126.5	3664.2

SOURCE: *Census of Manufacturers, 1977*, Dept. of Commerce, 1980.